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⑪ Publication number:

**0 567 964 A2**

⑫

## EUROPEAN PATENT APPLICATION

⑪ Application number: 93106721.9

⑤ Int. Cl.<sup>5</sup>: **B01D 53/36**

⑫ Date of filing: 26.04.93

③ Priority: 28.04.92 JP 109891/92  
20.01.93 JP 7703/93

④ Date of publication of application:  
03.11.93 Bulletin 93/44

⑧ Designated Contracting States:  
AT DE FR GB IT NL

⑦ Applicant: MITSUBISHI JUKOGYO KABUSHIKI  
KAISHA  
5-1, Marunouchi 2-chome  
Chiyoda-ku  
Tokyo(JP)

② Inventor: Morii, Atsushi, c/o Nagasaki Ship. &  
Mach. Works  
MITSUBISHI JUKOGYO K.K.,  
1-1, Akunoura-machi  
Nagasaki-shi, Nagasaki-ken(JP)  
Inventor: Kaneko, Shozo, c/o Nagasaki Ship. &  
Mach. Works  
MITSUBISHI JUKOGYO K.K.,  
1-1, Akunoura-machi  
Nagasaki-shi, Nagasaki-ken(JP)  
Inventor: Imamoto, Toshihiko, c/o Nagasaki  
Ship. & Mach. Works  
Mitsubishi Jukogyo K.K.,  
1-1, Akunoura-machi  
Nagasaki-shi, Nagasaki-ken(JP)

Inventor: Serizawa, Satoru, c/o Nagasaki  
Ship. & Mach. Works

MITSUBISHI JUKOGYO K.K.,

1-1, Akunoura-machi

Nagasaki-shi, Nagasaki-ken(JP)

Inventor: Naito, Osamu, c/o Nagasaki Ship. &  
Mach. Works

MITSUBISHI JUKOGYO K.K.,

1-1, Akunoura-machi

Nagasaki-shi, Nagasaki-ken(JP)

Inventor: Onishi, Toshiyuki, c/o Nagasaki  
Ship. & Mach. Works

MITSUBISHI JUKOGYO K.K.,

1-1, Akunoura-machi

Nagasaki-shi, Nagasaki-ken(JP)

Inventor: Kobayashi, Norihisa, c/o MITSUBISHI  
JUKOGYO K.K.

5-1, Marunouchi 2-chome

Chiyoda-ku, Tokyo(JP)

Inventor: Iida, Kouzo, c/o MITSUBISHI  
JUKOGYO K.K.

6-22, Kan-on-shinmachi 4-chome

Nishi-ku, Hiroshima-shi, Hiroshima-ken(JP)

⑦ Representative: Behrens, Dieter, Dr.-Ing. et al  
Wuesthoff & Wuesthoff  
Patent- und Rechtsanwälte  
Schweigerstrasse 2  
D-81541 München (DE)

⑤ Process for flue gas denitration.

⑦ A process for denitrating flue gas which comprises disposing a denitration catalyst bed using  $\text{NH}_3$  as a reducing agent in a region where the flue gas temperature ranges from 200 to 600 °C; injecting  $\text{NH}_3$  in an amount more than equimolar with nitrogen oxides in the flue gas at a point of the system upstream of the denitration catalyst bed and thereby removing  $\text{NO}_x$ ; and removing excess  $\text{NH}_3$  by adsorption at an  $\text{NH}_3$  adsorber which contains an  $\text{NH}_3$  adsorbent consisting of a metal oxide and having a specific surface area of at least 30  $\text{m}^2/\text{g}$  in a region downstream of the denitration catalyst bed where the flue gas temperature is 200 °C or below.

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## FIELD OF THE INVENTION AND RELATED ART STATEMENT

The present invention relates to a process for flue gas denitration.

5 Nitrogen oxides in flue gases have hitherto been removed by dry denitration systems using  $\text{NH}_3$  as a reducing agent. The rates of denitration attained today are no more than about 80 to 90 percent. Attempts to achieve higher efficiencies above 90 percent have been practically foiled by attendant increases in  $\text{NH}_3$  released into the atmosphere.

For controlling  $\text{NO}_x$  emission, dry denitration systems have been commonly used. The concentration of  $\text{NH}_3$  as a reducing agent at the exit of the denitration equipment usually has to be kept low in order to avoid  
10 both the waste of  $\text{NH}_3$  and its release in large quantity to the atmosphere. As a result, the denitration rate is limited to 80 to 90 percent at most.

## OBJECT AND SUMMARY OF THE INVENTION

15 The present invention, in view of the state of the art described above, is intended to provide a process whereby a dry denitration apparatus can achieve an efficiency as high as more than 90 percent.

The invention provides a process for denitrating flue gas characterized by the steps of installing a dry denitrator using  $\text{NH}_3$  as a reducing agent in a region of the system where the flue gas temperature ranges from 200 to 600 °C; injecting  $\text{NH}_3$  in an amount more than equimolar with nitrogen oxides in the flue gas at  
20 a point of the system upstream of the dry denitrator and thereby removing  $\text{NO}_x$ ; and locating an  $\text{NH}_3$  adsorber which contains an  $\text{NH}_3$  adsorbent consisting of a metal oxide and having a specific surface area of at least 30  $\text{m}^2/\text{g}$  in a region downstream of the dry denitrator where the flue gas temperature is 200 °C or below, whereby excess  $\text{NH}_3$  is removed by adsorption from the flue gas.

The invention provides also a process as defined above which is further characterized in that the  $\text{NH}_3$   
25 adsorbent consisting of a metal oxide and having a specific surface area of at least 30  $\text{m}^2/\text{g}$  comprises a metal oxide selected from the group consisting of zeolites, alumina, titania, silica, and zirconia.

By operating a denitration system so that the denitration reaction proceeds with an  $\text{NH}_3/\text{NO}_x$  (molar ratio) of more than 1, a larger amount of  $\text{NH}_3$ , which is a reducing agent, can be maintained with respect to that of  $\text{NO}_x$ . This ensures the contact of  $\text{NO}_x$  with  $\text{NH}_3$  and facilitates the  $\text{NO}_x$  removal. As a result, the  
30 constant excess of  $\text{NH}_3$  over  $\text{NO}_x$  leaves a substantial amount of unused  $\text{NH}_3$  at the exit of the denitrator. This buildup of the  $\text{NH}_3$  at the exit is undesirable because it leads to not only wasteful consumption of  $\text{NH}_3$  but also causes offensive smell and other problems when it is released to the atmosphere. For these reasons the  $\text{NH}_3$  must be removed by adsorption. Under the invention the  $\text{NH}_3$  at the exit of a denitrator is adsorbed away using an  $\text{NH}_3$  adsorbent consisting of a metal oxide and having a specific surface area of at  
35 least 30  $\text{m}^2/\text{g}$ . The  $\text{NH}_3$  adsorption performance of the  $\text{NH}_3$  adsorbent depends quite largely upon temperature, and favorable  $\text{NH}_3$  adsorption performance is realized at temperatures below 200 °C. A bed of the  $\text{NH}_3$  adsorbent is laid, therefore, in a location where it meets the flue gas at a temperature below 200 °C.

The  $\text{NH}_3$  adsorbent to be used in the present invention, which contains a metal oxide and having a  
40 specific surface area of at least 30  $\text{m}^2/\text{g}$ , comprises, for example, any of zeolites, alumina, titania, silica, or zirconia.

$\text{NH}_3$  that has been adsorbed by the  $\text{NH}_3$  adsorbent can easily be desorbed by heating the adsorbent above 200 °C. The desorbed  $\text{NH}_3$  is not a waste; it is reusable as a reducing agent. When the amount of the desorbed  $\text{NH}_3$  is too small for reuse, it is mixed with combustion air and burned off. There is no need  
45 for extra equipment for the disposal of  $\text{NH}_3$ .

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow diagram of an embodiment of the present invention;  
50 Fig. 2 is a flow diagram of another embodiment of the invention;  
Fig. 3 is a graph showing changes in the  $\text{NO}_x$  concentration in flue gas at the exit of a denitration reactor after the initiation of  $\text{NH}_3$  injection in conformity with the invention;  
Fig. 4 is a graph showing the relationship between the gas temperature for the  $\text{NH}_3$  adsorbent and the  $\text{NH}_3$  adsorption quantity ratio in Example 2 of the invention;  
55 Fig. 5 is a graph showing the results of adsorption-desorption tests on the  $\text{NH}_3$  adsorbent in Example 3 of the invention; and  
Fig. 6 is a graph showing the relationship between the gas temperature for the  $\text{NH}_3$  adsorbent and the  $\text{NH}_3$  adsorption quantity ratio in Example 4 of the invention.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Typical embodiments of the invention will now be described in detail with reference to Figs. 1 and 2, with further clarification of their operation.

In Fig. 1 is shown the flow diagram of a system for the denitration of flue gas and recovery of  $\text{NH}_3$ , including a boiler as a flue gas source. Fuel, air, and the like are introduced into the boiler 1 and burned, generating  $\text{NO}_x$ -laden flue gas. An  $\text{NH}_3$  injection nozzle 3 and a dry denitrator 4 which holds a denitration catalyst are connected to a flue gas duct at points downstream of the boiler 1. An air preheater 5 as a waste heat cooling or recovery means is located further downstream. The preheater effects heat exchange of the flue gas with combustion air 11 to lower the flue gas temperature below  $200^\circ\text{C}$ . Behind the preheater 5 is disposed an  $\text{NH}_3$  adsorber 7 which contains an  $\text{NH}_3$  adsorbent. The flue gas thus denitrated and stripped of  $\text{NH}_3$  is released through a stack 8 to the atmosphere.

The  $\text{NH}_3$  adsorber 7 is packed with an  $\text{NH}_3$  adsorbent consisting of a metal oxide and having a specific surface area of at least  $30\text{ m}^2/\text{g}$ . A separate line is formed to permit a hot gas to be introduced into the  $\text{NH}_3$  adsorber 7 through a hot gas inlet duct 10 to adjust the flue gas temperature to  $200^\circ\text{C}$  or above, preferably  $250^\circ\text{C}$  or above. Independently of the line extending to the stack 8, an alternative line is provided so that, when the hot gas is introduced, the gas forced out of the adsorber can be conducted by a damper and other parts not shown to a desorbed gas discharge duct 9.

Another system for flue gas denitration and  $\text{NH}_3$  recovery including a gas turbine as a flue gas generator will now be explained in connection with Fig. 2. As fuel, air, etc. are fed and burned together, the gas turbine 2 generates high-temperature  $\text{NO}_x$ -laden flue gas. On the downstream side of the gas turbine 2 installed are a dry denitrator 4 packed with a catalyst and which incorporates an array of ammonia spray nozzles 3, and a flue gas boiler 6. In the boiler heat exchange is effected with water to lower the flue gas temperature to  $200^\circ\text{C}$  or below. Other functions of the system are the same as those of the system illustrated in Fig. 1 and their description is omitted.

The present invention thus renders it possible to remove 99% or more  $\text{NO}_x$  from flue gas. In addition, it avoids wasteful consumption of  $\text{NH}_3$  used as a reducing agent.

## (Example 1)

In a gas flow rate of  $200\text{ Nm}^3/\text{h}$  and at a gas temperature of  $380^\circ\text{C}$ , a flue gas composed of 100 ppm  $\text{NO}_x$ , 14-15%  $\text{O}_2$ , and the remainder  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  was passed through an adsorber packed with a honeycomb catalyst made up of  $\text{TiO}_2$  (about 75%),  $\text{V}_2\text{O}_5$  (1%),  $\text{WO}_3$  (about 8%), and the remainder a bulking auxiliary agent so as to attain a space velocity (SV) of about  $10000\text{ h}^{-1}$ . The  $\text{NH}_3/\text{NO}_x$  (molar ratio) was varied from 0.8 to 0.9, 1.0, 1.1, and 1.2 and the denitration performances achieved were confirmed, the results being graphically represented in Fig. 3. The graph indicates the tendency that the normal value (10 ppm) is easily surpassed as the denitration rate rises beyond 90%.

## (Example 2)

An  $\text{NH}_3$  adsorbent was prepared in the form of 3 mm-dia. pellets consisting of 80% titanium oxide and the balance a bulking auxiliary agent. Samples then made had varying specific surface areas as given in Table 1.

Table 1

Sample	Specific surface area, $\text{m}^2/\text{g}$
A	2-3
B	15
C	30
D	50
E	80
F	120

The temperature dependence of the performance of the sample  $\text{NH}_3$  adsorbents was ascertained under the following conditions, the results being shown in Fig. 4.

Gas quantity : 400 Nl/h

Temperature : 100, 150, 200, 250, 300, and 450 °C

Flue gas composition:

$\text{NO}_x$  : 1 ppm

$\text{NH}_3$  : 20 ppm

$\text{O}_2$  : 14%

balance :  $\text{H}_2\text{O} + \text{N}_2 + \text{CO}_2$

$\text{NH}_3$  adsorbent: 3 mm-dia.  $\text{TiO}_2$ -base pellets, 20 cc

As can be seen from Fig. 4, the  $\text{NH}_3$  adsorption increases sharply at temperatures below 200 °C and with  $\text{NH}_3$  adsorbents having a specific surface area of 30  $\text{m}^2/\text{g}$  or more. In Fig. 4, the curves A to F represent the  $\text{NH}_3$  adsorbent samples shown in Table 1.

#### (Example 3)

A temperature swing test was conducted with 20 cc of an adsorbent having the same composition as above (80%  $\text{TiO}_2$  and the balance a bulking auxiliary agent, but with a specific surface area of 70  $\text{m}^2/\text{g}$ ) under the conditions given below. The test revealed that favorable adsorption-desorption properties are obtained as shown in Fig. 5.

Gas quantity : 400 Nl/h

Temperature : swung between 100 °C and 300 °C

Flue gas composition:

$\text{NO}_x$  : 1 ppm

$\text{NH}_3$  : 100 ppm

$\text{O}_2$  : 14%

balance:  $\text{H}_2\text{O} + \text{N}_2 + \text{O}_2$

$\text{NH}_3$  adsorbent: 3 mm-dia.  $\text{TiO}_2$ -base pellets, 20 cc

#### (Example 4)

An  $\text{NH}_3$  adsorbent consisting of 80% zeolite Y and 20% bulking auxiliary agent and another  $\text{NH}_3$  adsorbent consisting of 80% alumina and 20% bulking auxiliary agent were both pelletized to 3 mm-dia. pellets. Their adsorption characteristics were confirmed under conditions identical with those used in Example 3. The two  $\text{NH}_3$  adsorbents had specific surface areas of 500 and 200  $\text{m}^2/\text{g}$ , respectively. The results are shown in Fig. 6. As is clear from Fig. 6, the adsorption increased in both cases at temperatures below 200 °C.

Silica and zirconia, when employed as  $\text{NH}_3$  adsorbents, gave generally similar results.

#### Claims

1. A process for denitrating flue gas characterized by the steps of installing a dry denitrator using  $\text{NH}_3$  as a reducing agent in a region where the flue gas temperature ranges from 200 to 600 °C; injecting  $\text{NH}_3$  in an amount more than equimolar with nitrogen oxides present in the flue gas at a point upstream from the dry denitrator so as to remove  $\text{NO}_x$ ; and removing excess  $\text{NH}_3$  by adsorption at an  $\text{NH}_3$  adsorber which contains an  $\text{NH}_3$  adsorbent consisting of a metal oxide and having a specific surface area of at least 30  $\text{m}^2/\text{g}$  in a region which is downstream from the dry denitrator and where the flue gas temperature is 200 °C or below, whereby excess  $\text{NH}_3$ .
2. The process as claimed in claim 1, wherein the  $\text{NH}_3$  adsorbent consisting of a metal oxide and having a specific surface area of at least 30  $\text{m}^2/\text{g}$  comprises a metal oxide selected from the group consisting of zeolites, alumina, titania, silica, and zirconia.

FIG. 1

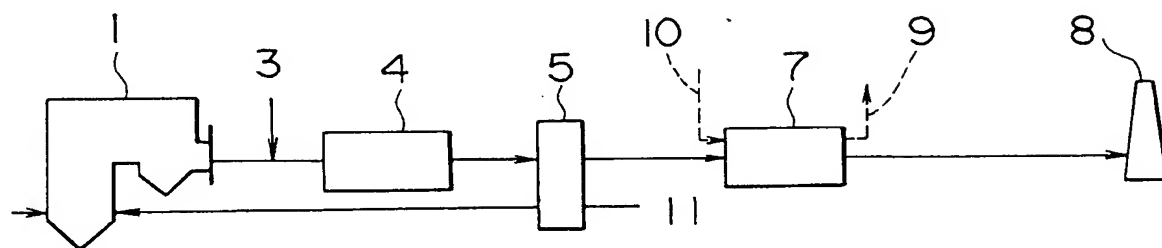


FIG. 2

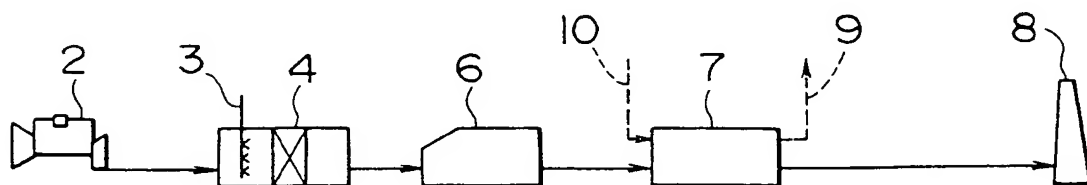


FIG. 3

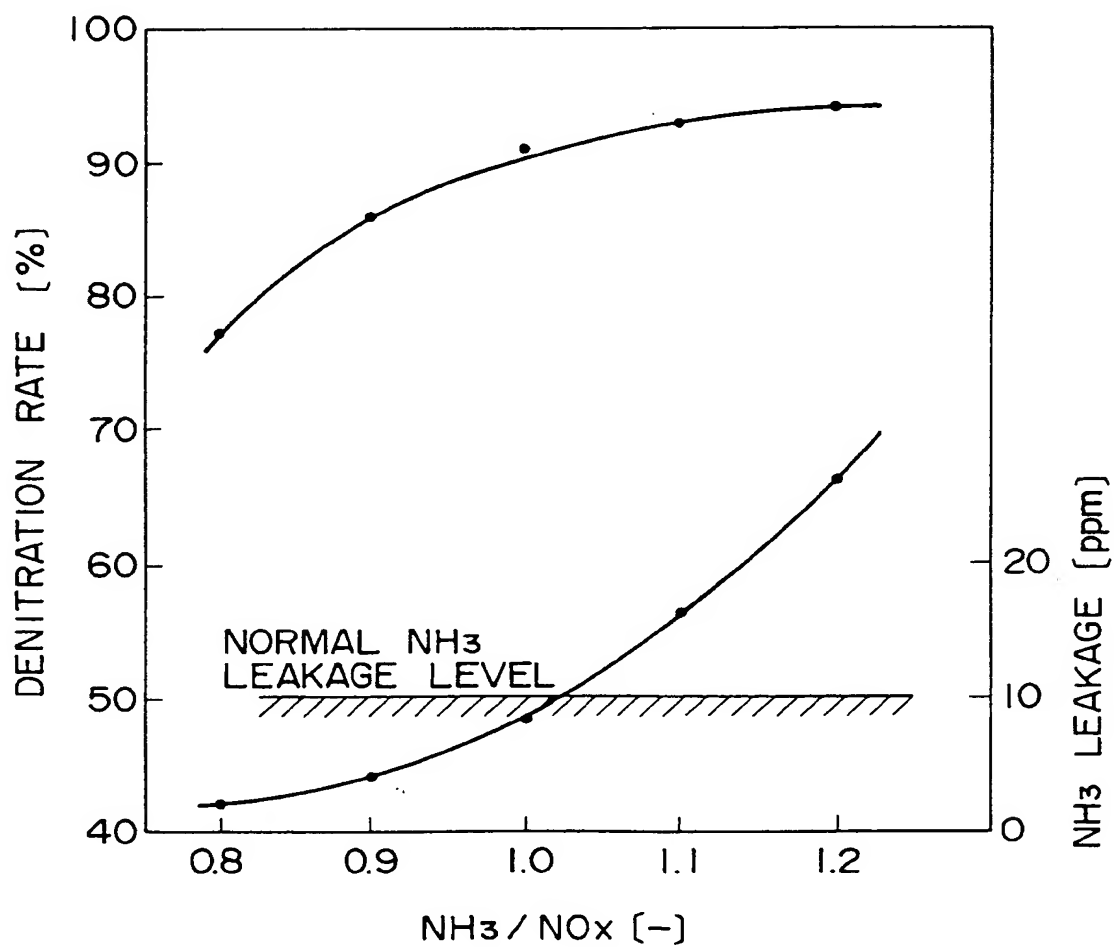


FIG. 4

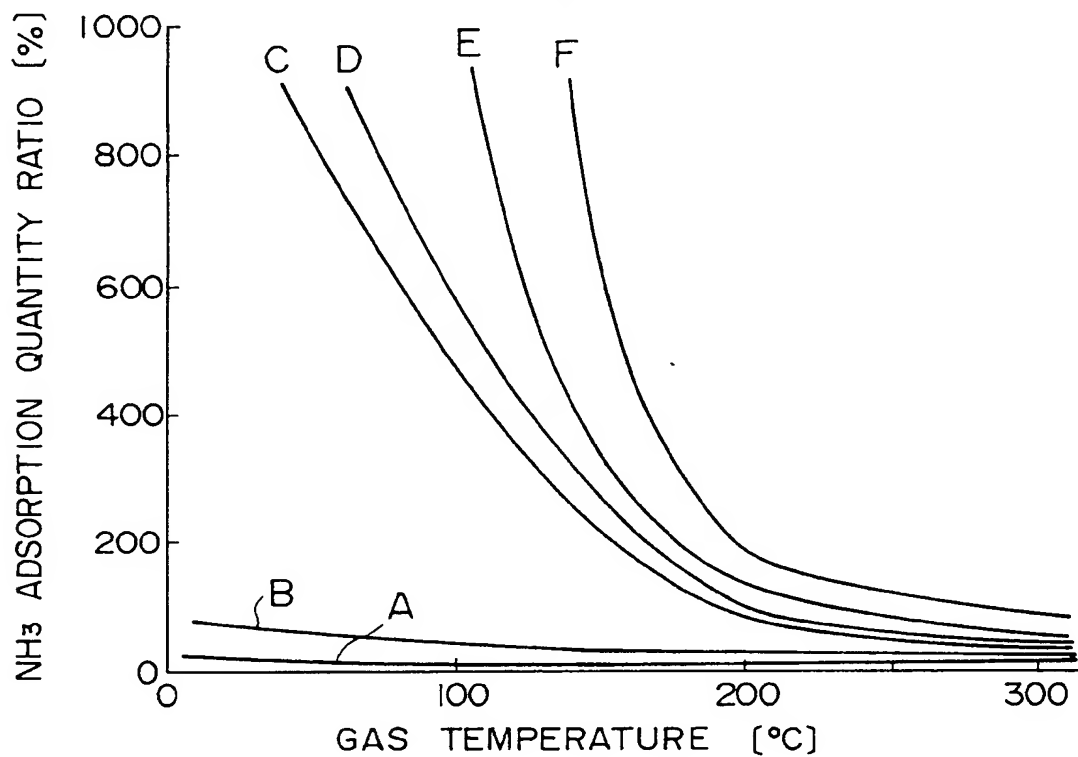


FIG. 5

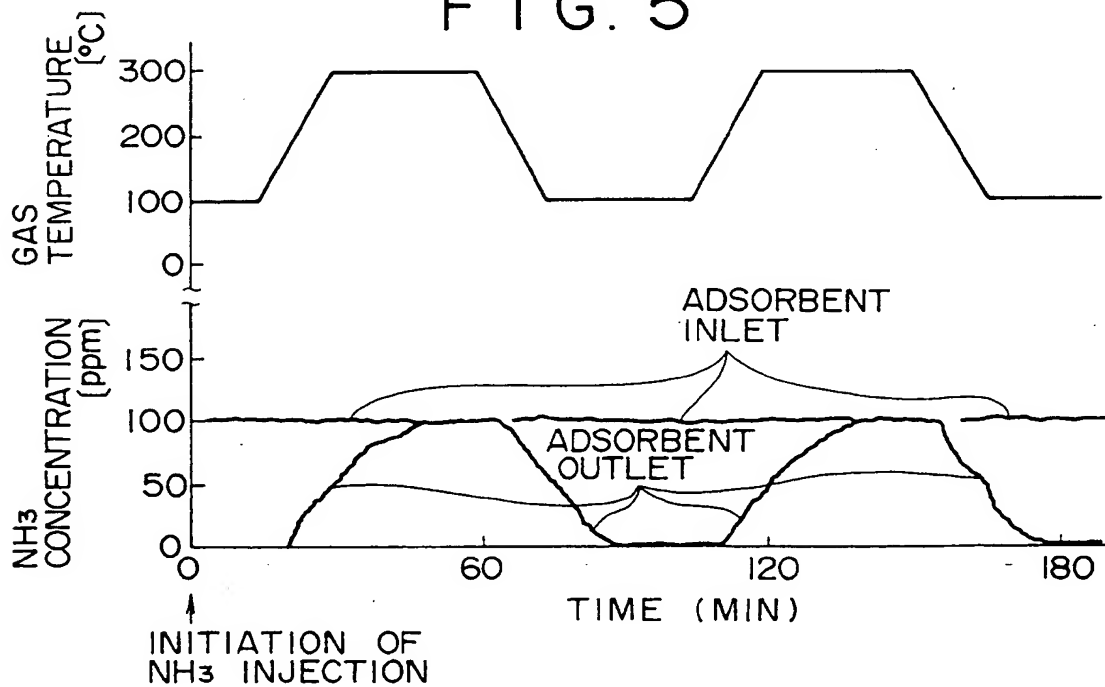
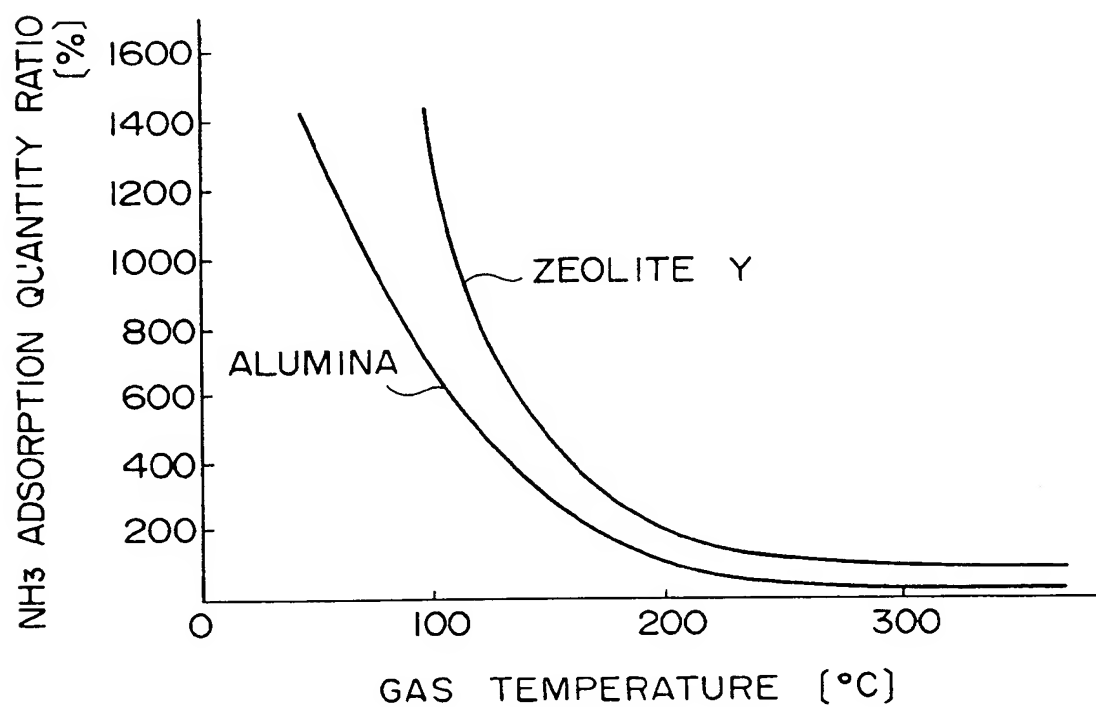


FIG. 6





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(11) Publication number:

**0 567 964 A3**

(12)

**EUROPEAN PATENT APPLICATION**(21) Application number: **93106721.9**(51) Int. Cl.<sup>5</sup>: **B01D 53/36**(22) Date of filing: **26.04.93**(30) Priority: **28.04.92 JP 109891/92**  
**20.01.93 JP 7703/93**(43) Date of publication of application:  
**03.11.93 Bulletin 93/44**(84) Designated Contracting States:  
**AT DE FR GB IT NL**(88) Date of deferred publication of the search report:  
**09.03.94 Bulletin 94/10**(71) Applicant: **MITSUBISHI JUKOGYO KABUSHIKI KAISHA**  
**5-1, Marunouchi 2-chome**  
**Chiyoda-ku**  
**Tokyo(JP)**(72) Inventor: **Morii, Atsushi, c/o Nagasaki Ship. & Mach. Works**  
**MITSUBISHI JUKOGYO K.K.,**  
**1-1, Akunoura-machi**  
**Nagasaki-shi, Nagasaki-ken(JP)**  
Inventor: **Kaneko, Shozo, c/o Nagasaki Ship. & Mach. Works**  
**MITSUBISHI JUKOGYO K.K.,**  
**1-1, Akunoura-machi**  
**Nagasaki-shi, Nagasaki-ken(JP)**  
Inventor: **Imamoto, Toshihiko, c/o Nagasaki Ship. & Mach. Works**  
**Mitsubishi Jukogyo K.K.,**

**1-1, Akunoura-machi**  
**Nagasaki-shi, Nagasaki-ken(JP)**  
Inventor: **Serizawa, Satoru, c/o Nagasaki Ship. & Mach. Works**  
**MITSUBISHI JUKOGYO K.K.,**  
**1-1, Akunoura-machi**  
**Nagasaki-shi, Nagasaki-ken(JP)**  
Inventor: **Naito, Osamu, c/o Nagasaki Ship. & Mach. Works**  
**MITSUBISHI JUKOGYO K.K.,**  
**1-1, Akunoura-machi**  
**Nagasaki-shi, Nagasaki-ken(JP)**  
Inventor: **Onishi, Toshiyuki, c/o Nagasaki Ship. & Mach. Works**  
**MITSUBISHI JUKOGYO K.K.,**  
**1-1, Akunoura-machi**  
**Nagasaki-shi, Nagasaki-ken(JP)**  
Inventor: **Kobayashi, Norihisa, c/o MITSUBISHI JUKOGYO K.K.**  
**5-1, Marunouchi 2-chome**  
**Chiyoda-ku, Tokyo(JP)**  
Inventor: **Iida, Kouzo, c/o MITSUBISHI JUKOGYO K.K.**  
**6-22, Kan-on-shinmachi 4-chome**  
**Nishi-ku, Hiroshima-shi, Hiroshima-ken(JP)**

(74) Representative: **Behrens, Dieter, Dr.-Ing. et al**  
**Wuesthoff & Wuesthoff**  
**Patent- und Rechtsanwälte**  
**Schweigerstrasse 2**  
**D-81541 München (DE)**(54) **Process for flue gas denitration.**

(57) A process for denitrating flue gas which comprises disposing a denitration catalyst bed using  $\text{NH}_3$  as a reducing agent in a region where the flue gas temperature ranges from 200 to 600 °C; injecting  $\text{NH}_3$  in an amount more than equimolar with nitrogen oxides in the flue gas at a point of the system upstream of the denitration catalyst bed and thereby removing  $\text{NO}_x$ ; and removing excess  $\text{NH}_3$  by adsorption at an  $\text{NH}_3$  adsorber which contains an  $\text{NH}_3$  adsorbent consisting of a metal oxide and hav-

ing a specific surface area of at least 30  $\text{m}^2/\text{g}$  in a region downstream of the denitration catalyst bed where the flue gas temperature is 200 °C or below.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 93 10 6721 .9

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
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Y	EP-A-0 469 593 (HALDOR TOPSOE A/S) * column 2, line 30 - column 4, line 21; claims 1-6; figure 1 *	1,2	
A	PATENT ABSTRACTS OF JAPAN vol. 005, no. 144 (C-071)11 September 1981 & JP-A-56 078 619 (MITSUBISHI KAKOKI KAISHA LTD) 27 June 1981 * abstract *	1	
A	EP-A-0 268 118 (RHEIN. BRAUNKOHLEWERKE AG) * column 5, line 21 - line 55; figure 1 *	1	
A	EP-A-0 264 041 (VON ROLL AG) * column 1, line 50 - column 4, line 7 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
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The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	11 January 1994	Eijkenboom, A	
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 150 (04.81) (P04C01)